Behavior of Liquid Metals on Ceramic Surfaces Explained

Eduardo Saiz, Antoni P. Tomsia, and Rowland M. Cannon in the CAM Ceramics Science Program, have made a major advance in understanding the behavior of liquid metals on ceramic surfaces. In doing so, they have solved a problem that has been perplexing scientists for 200 years.

The quantitative study of the interaction between a small amount of liquid and a surface (wetting) dates from the 19th century. Young and Dupré introduced the concept of the contact angle θ, (see figure) to measure the degree to which the liquid spreads (low contact angle), or beads (high contact angle). They also discovered that by considering the energies of the liquid/vapor, solid/vapor, and solid/liquid interfaces, they could derive a thermodynamic equation (Young-Dupré equation) that predicts the contact angle for a given system.

The Young-Dupré equation does not, however, accurately describe all wetting behavior. One of the most widely encountered of these exceptions is the observed hysteresis when a molten metal wets a surface at high temperature: the contact angles between droplets formed by advancing (growing) and receding (evaporating) liquids are different.

The understanding of this phenomenon is of both fundamental interest and practical value in controlling many important industrial processes, including soldering, brazing, coating, and composite processing. To study it, the research group performed experiments with a number of metals (nickel, copper, gold, aluminum) placed on alumina substrates at temperatures of up to 1600°C. The researchers then carefully studied the structure of the triple junction (see figure) formed where the molten liquid droplet, the solid surface, and the vapor from the droplet are in contact. To do this, they removed the metal droplets by acid etching, and then imaged the topography of the region with atomic force microscopy. They discovered that in cases where hysteresis was observed, the surface of the substrate in the triple junction region had not remained flat. Instead they found small ridges ranging in height from a few to several hundred nanometers.

Since the Young-Dupré equation assumes that the substrate is rigid and insoluble, the presence of ridges could be the basis for the hysteresis in high-temperature wetting. The group further determined that the ridges are formed by diffusion of substrate material under the metal droplet. The rate of this diffusion increases with temperature. The group calculated that deviations from the Young-Dupré equation can be expected whenever the temperature is above 1/4 of the melting point of the substrate. The group further showed that the shapes of ridges formed by advancing and receding metal fronts are different and they developed a quantitative theory of high-temperature wetting that correctly accounts for substrate diffusion and explains why spreading rates are often orders of magnitude slower than found in low temperatures systems.

This study has resolved decades-old debates about the theoretical basis of the Young-Dupré equation and the predictability of wetting processes, and has significantly increased our understanding of wetting. The new theory has revealed that there are limiting conditions under which the Young-Dupré equation is correct and can be used to measure interfacial energies or adhesion forces for high temperature systems. It also provides a basis for new theories describing the dynamics of wetting under other, more general conditions.

Antoni P. Tomsia (510) 486-4918. Materials Sciences Division (510) 486-4755, E. O. Lawrence Berkeley National Laboratory.

E. Saiz, A. P. Tomsia, and R. M. Cannon, Reactive Spreading: Adsorption, Ridging and Compound Formation, *Acta Materialia*, **48**, No. 18-19, 4449–4462 (2000).

E. Saiz, A. P. Tomsia, and R. M. Cannon, Triple Line Ridging and Attachment in High Temperature Wetting, *Scripta Materialia*, **44** [1] 159–164 (2001).